Effect of salt additives on decolouration of Acid Black 1 dye effluent by ozonation

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An attempt was made to study the effect of presence of inorganic salts namely, sodium carbonate, sodium chloride and sodium sulphate, and their concentrations on decolouration of acid dye effluent by ozonation. Studies have been conducted at different salt concentrations and at alkaline pH on Acid Black 1 dye effluent, having a concentration of 500 µM. It has been found that salt content in the effluent increases the decolouration time of the acid dye effluent. Higher the salt content more is the decolouration time and among the salts, sodium carbonate requires more time for complete decolouration than the sodium chloride and sodium sulphate. Chemical oxygen demand (COD) reduces by 52, 58 and 62% whereas total organic carbon (TOC) reduces by 28, 32 and 33% for the salt present in the effluent, namely sodium carbonate, sodium chloride and sodium sulphate respectively. IR spectra study confirms the formation of acidic by-products during ozonation.

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Salts form a major component in the application of various dyes on textiles. They are used as exhausting agents for applying direct dyes on cellulose fibres, acid milling dyes on wool, reactive dyes on cotton, etc., and as retarding agents for applying leveling dyes on wool, basic dyes on acrylic, etc. The commonly used salts for this purpose are sodium chloride and sodium sulphate. The quantity of these salts required for the dyeing varies with the chemical nature of the dye used. In general, the quantity required may vary from 5 to 10 g/L. The addition of salt in the dye bath invariably increases the pollution load of the effluent generated, which in turn affects the effluent treatment process.

A number of attempts have been made for the treatment of wastewater using oxidation techniques. The studies carried out using chlorine and its derivatives1,2, hydrogen peroxide in the presence of iron(II) salts known as Fenton’s reagent3, ozone4,5, UV radiation combined with ozone6,7, and/or hydrogen peroxide8,9 and electrochemical cells10,11 are a few among them.

A number of studies have been carried out on ozone treatment of effluent in presence of additives. The use of additives such as silicone type antifoaming agents, salt, sodium silicate, surfactants, thickeners and urea in reactive dye bath, chelating agents such as ethylene diamine tetra acetic acid (EDTA), diethylene triamine penta acetic acid (DTPA) in disperse dyebath on ozonation has been reported14-16. A brief mention about the effect of salt during ozone decolouration of reactive dye effluent is also reported17. But the author did not discuss about the nature and quantity of the salt used in their study.

Hence, a study was made to find the effect of additives such as sodium sulphate, sodium chloride and sodium carbonate on decolouration of acid dye effluent by ozone. Studies were conducted at two different alkaline pH on dye effluent, using Acid Black 1 dye with a concentration of 500 µM. It was found from the literature that alkaline pH favours the faster decolouration of dye effluent than acidic and neutral pH on ozonation. So pH 9 and 11 were selected in the present studies. Effect on chemical oxygen demand and total organic carbon content reduction were also studied.

Experimental Procedure

Materials

Acid dye C.I. Acid Black 1, was obtained from Atul Limited, India (Fig. 1). The dye was used as obtained. The salts, sodium carbonate, sodium chloride, and sodium sulphate of analytical grade (Qualigens Fine Chemicals, India) were used.
Experimental set-up

The experimental set-up (Fig. 2) consisted of an oxygen concentrator (Sim O₂ plus, Italy), ozone generator (Ozonetek Ltd., India), ozonation chamber and ozone destructor (Ozonetek Ltd., India). A controlled flow rate of 2 L/min of oxygen was used to produce 2 g/h of ozone. The concentration of ozone was analysed using an ozone analyzer (BMT 201, Berlin). The ozonation chamber consisted of 1500 mm glass column with 50 mm inner diameter having a capacity to hold 850 mL of effluent. It was provided with a sample port at various points, an ozone gas inlet at the bottom with a ceramic diffuser over the inlet port to diffuse the oxygen/ozone gas mixture through the column and a closed top with a collection port to collect the unreacted ozone gas for analysis and to the thermal vent ozone destructor before venting it out. A PTFE tube was used for connecting the ozone outlet port from the ozone generator to the ozone reaction chamber.

Parameters analyzed

Effluents (500 mL) having a concentration of 500 μM of dye were used for treatments. Decolouration of the dye effluent by ozone was determined at frequent intervals through absorbance at maximum wavelength (λ_{max}) of the dye (619 nm) using Hitachi UV-Visible spectrophotometer (U-3210), Japan. Before and after treatment, pH of the effluent was determined using pH meter (Systronics μ pH system 361, India). Chemical oxygen demand (COD) was analyzed by using open reflux method^{18} and total organic carbon content (TOC) was determined by TOC analyzer (Micro N/C 1997, Analytica Jena, Germany). The identification of by-products produced during ozonation of the effluent was assessed by IR studies. The IR spectrum of the sample was recorded using Perkin-Elmer 781 Fourier transform infrared spectrophotometer, Germany, using the samples in liquid form.

Results and Discussion

Effect of salts on decolouration of dye effluent

The effect of presence of salts such as sodium sulphate, sodium chloride and sodium carbonate on the decolouration of Acid Black 1 dye effluent by ozone was studied using 10 g/L of the dye solution by adjusting the pH at 9 and 11. Fig. 3 shows the effect of presence of salt on decolouration of Acid Black 1 dye effluent at pH 9 and 11. It is observed from the figure that the complete decolouration time is least when the effluent contains no salt in it, irrespective of their pH levels. It can also be seen from the figure that, the complete decolouration time required is lower when sodium sulphate is present in the effluent than that of the presence of sodium chloride and sodium carbonate at any given pH. It is stated that sodium sulphate undergoes dissociation as follows:

\[ \text{Na}_2\text{SO}_4 \leftrightarrow 2\text{Na} + \text{SO}_4^{2-} \]  … (1)
In alkaline pH, ozone is decomposed to produce OH°, the reactions (2) – (5) can take place:

\[
\text{SO}_4^{2-} + \text{OH}^\circ \rightarrow \text{SO}_4^{\circ-} + \text{OH}^- \quad \ldots (2)
\]

\[
2\text{SO}_4^{\circ-} \rightarrow \text{S}_2\text{O}_8^{2-} + 2 \text{e}^- \quad \ldots (3)
\]

\[
\text{SO}_4^{\circ-} + \text{dye} \rightarrow \text{SO}_4^{2-} + \text{dye}^{\circ+} \quad \text{(intermediate)} \quad \ldots (4)
\]

\[
\text{SO}_4^{\circ+} + \text{dye}^{\circ+} \quad \text{(intermediate)} \rightarrow \text{SO}_4^{2-} + \text{CO}_2 + \text{other inorganics} \quad \ldots (5)
\]

The oxidation potential of sulphate radical anion is 2.01 V. It is higher than the oxidation potential of hypochlorous acid (1.5 V), hypochloric ion (0.89 V), chlorine dioxide (1.15 V) and chlorine (1.36 V)\textsuperscript{12}, which are produced during dissociation of sodium chloride in the dye effluent at alkaline pH. Moreover, the SO\textsubscript{4}^{\circ-} has a unique nature of attacking the dye molecule at various positions resulting in rapid fragmentation of the dye molecules\textsuperscript{20} leading to the faster decolouration of the dye effluent.

The carbonate and bicarbonate ions are thought to react with OH radicals as given in reactions (6) – (8) indicating that the carbonate radical anion is a weak oxidising agent that hardly reacts with other molecules\textsuperscript{21}. Also the presence of bicarbonates in the effluent may inhibit the free radical reaction chain, hence slowing down decomposition of ozone in the effluent\textsuperscript{22}.

\[
\text{CO}_3^{2-} + \text{OH}^\circ \rightarrow \text{CO}_3^{\circ-} + \text{OH}^- \quad \ldots (6)
\]

\[
\text{HCO}_3^- + \text{OH}^\circ \rightarrow \text{CO}_3^{\circ-} + \text{H}_2\text{O} \quad \ldots (7)
\]

\[
\text{CO}_3^{\circ-} + \text{O}_3 \rightarrow \text{CO}_2 + 2 \text{O}_2 \quad \ldots (8)
\]

The inhibitors of the free radical reaction are compounds capable of consuming OH radicals without regenerating the super oxide anion O\textsubscript{2}^-.

Thus, it can be said that the presence of sodium carbonate and sodium chloride in the effluent results in higher reduction in the efficiency of the decolourisation process by ozone compared to that of sodium sulphate. Optimum pH was found to be 9 because with increasing pH to 11 more number of OH radicals were produced which react with other OH radicals to form hydrogen peroxide rather than reacting with target compounds.

**Effect of salt concentration on decolouration**

The above study clearly indicates that complete decolourisation reaction is faster at pH 9 than at pH 11.

Based on this, pH 9 was used to study the effect of selected concentration of salt (5, 10 and 15 g/L) on decolourisation of the Acid Black 1 dye effluent by ozone. The results are shown in Figs 4-6. The time taken for complete decolouration (given in Table 1) shows when the concentration of salt increases, decolouration time increases.

Namboodri et al.\textsuperscript{15} have studied the effect of additives (EDTA) on decolourisation of disperse red 60 and reported, that, an
increasing concentration of EDTA in the dye bath causes proportional increase in the time required for colour removal. This trend was observed not only with EDTA but also with levelling agents and/or defoamer present in the dye bath. Carriee et al.\textsuperscript{16} reported that increasing the auxiliaries (gaur gum) concentration in the dye solution increases the amount of ozone required to achieve complete decolouration. Ghar et al.\textsuperscript{17} also have reported that water glass accelerates decolouration and salt influences the decolouration but it decreases with increasing pH. However, the author doesn’t mention the nature of salt used. In this study, it was found, that, increasing salt concentration in dye solution increases the decolouration time. This can be attributed to the lower reaction rate kinetics of ozone with dye in the presence of a salt due to intermediate negative ion formation, which reacts with ozone and increases the ozone consumption, thus increasing the decolouration time.

**Effect on COD**

The COD removal was studied in the effluents by varying pH 9 and 11 and at a salt concentration of 10 g/L. It was observed that the change of pH had little effect on the COD removal as shown in Table 2. The maximum removal of COD was 52, 58 and 62% for sodium carbonate, sodium chloride and sodium sulphate respectively. The reduction of COD is due to the reduction of total organic carbon (TOC) and partial oxidation of organic substrates. Similar observation was made by Lopez et al.\textsuperscript{23}, who have observed a reduction of COD in their study on ozone treatment of industrial textile effluents. Koynnchu and

### Table 1—The time taken for complete decolouration of Acid Black 1 dye effluent in presence of different salts and its concentration at pH 9

<table>
<thead>
<tr>
<th>Salt conc. (g/L)</th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Na\textsubscript{2}SO\textsubscript{4}</td>
<td>NaCl</td>
<td>Na\textsubscript{2}CO\textsubscript{3}</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>9</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>15</td>
<td>11</td>
<td>13</td>
<td>16</td>
</tr>
</tbody>
</table>

### Table 2—Effect of pH and salts on COD and TOC removal

<table>
<thead>
<tr>
<th>Salt (10 g/L)</th>
<th>% COD removal</th>
<th>% TOC removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 9</td>
<td>pH 11</td>
</tr>
<tr>
<td>Na\textsubscript{2}SO\textsubscript{4}</td>
<td>59</td>
<td>61</td>
</tr>
<tr>
<td>NaCl</td>
<td>58</td>
<td>56</td>
</tr>
<tr>
<td>Na\textsubscript{2}CO\textsubscript{3}</td>
<td>48</td>
<td>52</td>
</tr>
</tbody>
</table>

**Effect on TOC**

The TOC removal was studied using the conditions as described in COD removal. The results are given in Table 2. It is found from the table that the treatment of dye effluents with ozone resulted in reduction of TOC content, which is due to the oxidation of organic carbon in to CO\textsubscript{2} and/or carbonates. The results also show that TOC reduction was not significant by
varying the pH. However at pH 9, TOC reduction was less when compared with pH 11. The reduction of TOC is around 33% with sodium sulphate added dye bath effluent, whereas it is 32 and 28% in sodium chloride and sodium carbonate added dye effluent respectively. The poor TOC reduction has also been reported in the treatment of textile/domestic combined wastewater.

Conclusion

It can be concluded from the above studies that the presence of salt in the effluent increases the decolouration time and pH of 9 favours a faster decolouration rate irrespective of the salt used. Comparing different types of salts, sodium sulphate present in the effluent increases the decolouring efficiency of ozone than that of sodium chloride and sodium carbonate in the effluent. Higher COD reduction was found in the effluent containing sodium sulphate, compared to the effluents containing sodium chloride and sodium carbonate salts. Decrease in pH of the effluent after ozonation, might be due to the formation of acetic by-products. Reduction in TOC was observed in effluent, in the following order—sodium sulphate > sodium chloride > sodium carbonate.

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References